

Encapsulated Metal Hydride Separation Membrane Development

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Objectives

- Produce a sol-gel encapsulated metal hydride packing material that will absorb hydrogen selectively, will not break down to fines, and will tolerate reactive impurities.
- Evaluate the packing material for hydrogen absorption from low concentration streams.
- Develop separation process with the new packing material.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- AB.Hydrogen Separation and Purification

Approach

- Develop formulations and procedures to make silica encapsulated metal hydride composite material.
- Design and install gas manifold for testing encapsulated packing materials for hydrogen absorption from streams of gas mixtures. The tests will generate hydrogen capacity and absorption kinetic data.
- Analyze the encapsulated packing materials before and after repeated hydrogen absorption and desorption to evaluate their physical stability.
- Develop process to use this new hydrogen absorption packing material for efficient hydrogen separation from low concentration gas streams.

Accomplishments

- Produced five variations of encapsulated samples for hydrogen absorption test.
- Conducted hydrogen absorption tests with various samples from gas mixtures that contain nitrogen, methane and carbon monoxide.
- Developed new encapsulation technique that significantly improved the physical stability of the product.

Future Directions

- Increase metal hydride content in the encapsulated product to maximize hydrogen capacity.
- Investigate the encapsulation of metal hydrides of higher equilibrium hydrogen pressure so that the product is better suited for use in pressure swing absorption separation processes.
- Optimize the porosity of the encapsulating matrix to increase the product's resistance to reactive impurities.

- Design and fabricate a pressure swing absorption experimental apparatus to test the encapsulated metal hydride for hydrogen separation.
- Conduct cost analysis.

Introduction

Hydrogen is certainly a clean fuel, but there is no significant quantity of naturally free hydrogen anywhere on earth. Hydrogen exists mostly in combined form with other elements, such as in water and hydrocarbons. Energy is required to free hydrogen from these compounds before it can be used as a fuel. This energy requirement must be minimized to maximize the net useful energy carried by hydrogen. Hydrogen demand today is mostly from the chemical industry and the petroleum refinery industry. This demand for hydrogen is met by steam reforming of natural gas and partial oxidation of hydrocarbon liquids and coal. The cost of hydrogen produced in this way is very low compared to the value of the products made. Many off-gas streams containing up to 50% hydrogen are discarded for economic reasons. Besides, hydrogen produced today is only a few percent of overall energy demand.

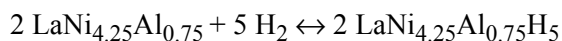
A hydrogen economy will bring many changes. First, hydrogen demand will increase many fold. Second, hydrogen will be produced from multiple sources that include renewable and non-renewable. Third, low hydrogen content streams will not be discarded, and the hydrogen must be recovered using cost-effective recovery techniques.

Present technologies for hydrogen separation include pressure swing adsorption (PSA), liquefaction, and membranes. All three processes are efficient for high hydrogen contents and high-pressure feeds but are not efficient for low hydrogen contents and low-pressure feeds. For PSA, the inefficiency is partly due to the fact that the absorbents, including molecular sieves and activated carbons, preferentially absorb the heavy impurities. This is good if the heavy impurities are less than 50%, but is not as good otherwise. When hydrogen content in a gas mixture is less than about 50%, it is more efficient to use an absorbent that absorbs

hydrogen instead of the heavier components. A hydrogen absorbent that can be used in a practical separation process is not available today. The objective of this project is to develop such an absorbent and the process to use it.

Approach

Metal hydrides are a very well known group of materials that absorb hydrogen reversibly at moderate conditions. One example is $\text{LaNi}_{4.25}\text{Al}_{0.75}$:



Each bulk liter of this material can absorb up to 18 moles of hydrogen reversibly. The hydrogen can be absorbed and desorbed by changing the hydrogen pressure, the temperature or both. This group of materials would have been well suited for hydrogen recovery from low concentration streams if not for two practical problems. First, metal hydrides in general break down to fines after repeated hydrogen absorption and desorption. The fines are in the micron range that makes them very difficult to use in separation columns. Second, metal hydrides are sensitive to reactive impurities like oxygen and carbon monoxide. Low levels of these impurities can render metal hydrides inactive toward hydrogen. Past efforts to deal with these problems are described by the works of Sandrock et al [1] and Suda et al [2].

In this work, a metal hydride is first broken down to fine particles. The fine particles are then encapsulated in a porous silica matrix to form a composite material. The composite is made in the form of granules or beads for packing separation columns. Each granule is a matrix of porous silica with metal hydride particles uniformly distributed in it. The porosity of the matrix permits hydrogen to reach the metal hydride particles but prevents the larger impurity molecules from penetrating. The porous matrix is strong and has void space for the metal hydride particles to expand and contract so that

hydrogen absorption and desorption do not cause breakage of the granules. The composite granules can therefore withstand hydrogen absorption/desorption without generating fines and have good tolerance to reactive impurities.

The encapsulated metal hydride samples are tested for hydrogen absorption first in a batch mode, then in a flow-through mode. In the flow-through mode, a small column is packed with the encapsulated metal hydride granules. Gas mixtures of hydrogen in nitrogen containing methane or carbon monoxide are fed into the column. Hydrogen concentration at the column exit is measured so that breakthrough curves are generated. The breakthrough curves give the capacity and kinetic information of the absorbent at the experimental conditions. The column is regenerated by heat and purging with nitrogen after hydrogen breaks through. After repeated absorption and desorption, the encapsulated granules are inspected for their physical conditions visually and microscopically. Success of a sample is defined by its ability to maintain its hydrogen capacity, absorption kinetics, and physical integrity after repeated cycling. Longer term, a pressure swing separation process using the encapsulated metal hydride (MH) as a packing material will be developed and demonstrated.

Results

Five different encapsulation methods were investigated that generated samples for hydrogen absorption tests: (1) Fumed silica was used for the porous matrix that encapsulated the fine particles of lanthanum-nickel-aluminum ($\text{LaNi}_{4.25}\text{Al}_{0.75}$); (2) Tetraethyl orthosilicate (TEOS) sol-gel was used as the source of silica for the matrix; (3) Sample in (1) was further treated with TEOS; (4) Method was the same as in (1) except that the La-Ni-Al particles were fluorinated [2] before encapsulation; (5) A method called external gelation that combined fumed silica, TEOS, and pore former to encapsulate the La-Ni-Al powder was used. The samples were tested for hydrogen absorption from different mixtures. Their hydrogen capacities and ability to withstand repeated absorption/desorption cycles are summarized in Table 1. The results show that good resistance to attrition is achieved by most of the samples. The presence of methane does not reduce the hydrogen capacity. The presence of carbon monoxide reduces the capacity significantly. One of the future efforts will be to improve the resistance toward CO.

Figures 1 to 4 show photographs of encapsulated metal hydride samples and the original metal hydride particles before and after hydrogen absorption/desorption cycling. The granules and beads of

Table 1: Summary of Test Results

Method	Resistance to attrition	H ₂ capacity from N ₂ stream mmol/g MH	H ₂ capacity from (N ₂ +10% CH ₄) mmol/g MH	H ₂ capacity from (N ₂ +1% CO) mmol/g MH
Fume silica + $\text{LaNi}_{4.25}\text{Al}_{0.75}$	good	5	to be tested	to be tested
TEOS sol-gel + $\text{LaNi}_{4.25}\text{Al}_{0.75}$	poor	2	to be tested	0.45
Fume silica + $\text{LaNi}_{4.25}\text{Al}_{0.75}$ + TEOS	good	4.5	4.5	1.7
Fumed silica + fluorinated $\text{LaNi}_{4.25}\text{Al}_{0.75}$	good	4	to be tested	0.45
External gelation + pore former + $\text{LaNi}_{4.25}\text{Al}_{0.75}$	very good	4	to be tested	to be tested

encapsulated metal hydride stay intact after repeated hydrogen absorption/desorption cycling. On the contrary, metal hydride particles by themselves break down to a fine powder after a few cycles.

In flow-through tests, a 40-cc sample is loaded in a $\frac{3}{4}$ -inch diameter, 6-inch long column that is installed on a gas manifold. A feed stream of low concentration hydrogen in nitrogen is delivered to the column. Methane or carbon monoxide is added to the feed depending on the test plan. Hydrogen is absorbed by the encapsulated metal hydride. Nitrogen and other impurities just pass through the column. Hydrogen concentration measured at the exit of the column is very low at the beginning and

increases gradually when the metal hydride becomes saturated, producing a breakthrough curve. The breakthrough curve provides information on the performance of the sample. To regenerate, the column is heated to 120°C and purged with nitrogen. From the hydrogen concentration measured at the exit, the partial pressure and quantity of hydrogen recovered can be calculated. A typical set of breakthrough curve and regeneration results are shown in Figure 5. The feed gas contained 12% hydrogen in nitrogen. The feed flow rate was 34 standard cc per minute. The pressure was 1500 torr (29 psia), and the temperature was 22°C. The column absorbed more than about 90% of the hydrogen for about 300 minutes before the hydrogen



Figure 1. Encapsulated La-Ni-Al after 100 Cycles



Figure 3. Metal Hydride Particles before Cycling



Figure 2. Encapsulated La-Ni-Al by External Gelation Method



Figure 4. Metal Hydride Particles after 10 Cycles

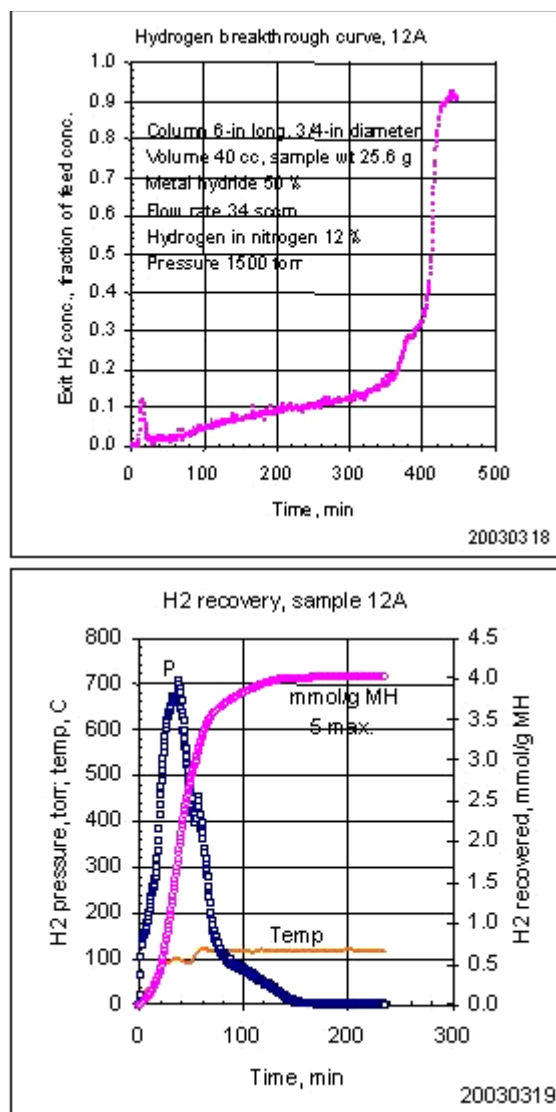


Figure 5. Breakthrough Curve (Top) and Regeneration Results (Bottom) of Hydrogen Absorption by Encapsulated Metal Hydride

broke through rapidly at about 400 minutes into the run. During regeneration, the partial pressure of hydrogen increased with temperature until it reached a maximum of 700 torr. The total hydrogen recovered was about 4 mmol/g of metal hydride compared to a maximum of about 6 at equilibrium.

Conclusions

- Metal hydride powder can be encapsulated in a porous silica matrix using a variety of techniques to produce stable granules suitable for hydrogen separation.
- The encapsulated metal hydride retains its ability to absorb hydrogen readily and has better resistance to reactive impurities.
- The external gelation technique combining the use of a pore former produces the strongest granules. The resistance of these granules to reactive impurities needs to be tested.
- Breakthrough curve data show that an effective pressure swing, temperature swing, or combination swing process for hydrogen recovery from low concentration streams can be developed.

References

1. J. J. Sheridan III et al, Journal of the Less-Common Metals, 89 (1983) 447-455
2. X.-L. Wang et al, Journal of Alloys and Compounds, 231 (1995) 860-864

FY 2003 Publications/Presentations

1. Paper titled "Hydrogen Absorption Property of Encapsulated $\text{LaNi}_{4.25}\text{Al}_{0.75}$ " was accepted for presentation at HYPOTHESIS V (Hydrogen Power - Theoretical and Engineering Solutions International Symposium) to be held 7-10 September, 2003.

Special Recognitions & Awards/Patents Issued

1. U.S. patent number 6,528,441 was issued on March 4, 2003.